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ADSORPTION OF ESTRONE ON NF AND RO MEMBRANES IN WATER AND WASTEWATER TREATMENT

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ABSTRACT

Adsorption of the trace contaminant estrone, a natural hormone and commonly abundant in surface waters and in treated as well as untreated wastewaters, to eight commercial nanofiltration (NF) and reverse osmosis (RO) membranes was investigated under well-defined conditions. Experiments were conducted in stainless steel stirred cells by spiking trace levels (100ng.L^{-1}) of estrone into five different matrices, namely MilliQ water, a bicarbonate solution, synthetic natural waters containing natural organics, and secondary effluent. Results show that estrone is adsorbed to the membranes to varying degrees with extent of adsorption influenced by the feedwater composition with different mechanisms of association controlling adsorption to different membrane types. Increase in membrane resistance is typically observed to result in decrease in extent of estrone adsorption.

KEYWORDS

Endocrine disrupter, estrone, hormone, adsorption, nanofiltration (NF), reverse osmosis (RO), natural organic matter (NOM), wastewater treatment, water treatment.

INTRODUCTION

Endocrine disrupters are compounds that can alter functions of the endocrine system and consequently cause adverse health effects to humans and animals. Amongst the large range of endocrine disrupting chemicals known to exist, two naturally occurring hormones (estrone and 17ß-estradiol) and a synthetic hormone (17β-ethinylestradiol) have the highest endocrine disrupting potential. Being excreted by humans, they are abundant in wastewater with concentrations ranging between non-detectable and 1 µg/L (Stumpf et al, 1999). In contrast, only 1 ng/L of estrogens need to be present to show definite effects in fish in laboratory experiments (Purdom et al. 1994). Both secondary effluent and surface waters may contain endocrine disrupters (Ternes et al. (1999). We have chosen the natural hormone estrone for study in this work.

Our previous work shown that reverse osmosis (RO) and nanofiltration (NF) membranes have a high potential to remove natural estrogenic compounds from aqueous solution (Schäfer et al, (submitted B)). Estrone can form hydrogen bonds with membranes resulting in adsorption to the membranes. If adsorption is the main mechanism by which estrone is retained, retention may be limited by the availability of interactive sites. In addition, little is known of the effect of various solution components on the extent and nature of uptake and the possibility also exists that, on change in solution conditions, rapid release from the membrane may occur. In order to elucidate some of these issues, we have investigated the adsorption of estrone to selected membranes in

various solutions including MilliQ water, a bicarbonate solution, synthetic natural waters containing natural organics and secondary effluent and report the results of these studies here.

BACKGROUND

Water and wastewater treatment using membrane processes often requires the removal of trace organics yet the actual mode of removal is often far from clear. Sorption of the trace organic to hydrophobic components of the membrane may occur as may specific interactions with hydrophilic sites and electrostatic interactions with membrane charged functional groups (Williams et al., 1999). Adsorption of trace organics on the membrane not only can influence the concentration in the retentate but also the extent of retention. Kiso et al. (2000 and 2001) investigated the retention of a number of pesticides and mono-substituted benzenes and alkyl phthalates by nanofiltration membranes and all of these compounds were found to be strongly adsorbed to the membranes.

While the pore transport model is useful for inorganic solute separation, models of trace organics interaction with membranes are more commonly based on diffusion and adsorption processes (Williams et al., 1999). Recently, Chen et al. (2001) developed a new model based on the diffusion of small molecule which penetrate into dense polymer membranes. In this model, the mass transport process consists of three consecutive steps: (i) sorption of the molecule from the feed solution to the membrane; (ii) diffusion of the molecule in the membrane; and (iii) desorption of the molecule from the membrane to solution on the downstream side of the membrane. Further consideration is given to these key processes later in this paper when discussing the results of studies of estrone retention by NF and RO membranes.

The chemical and physical characteristics of estrone are described in detail elsewhere (Schäfer et al., submitted B). Estrone is a hydrophobic compound with a relatively high octanol-water partitioning coefficient (log P) and a very low solubility in water. Its hydroxyl and carbonyl functional groups make it capable of participating in H-bonding both as a proton-donor and proton-acceptor species. The compound is uncharged in the pH range of most natural waters and wastewaters.

MATERIALS AND METHODS

Membranes

Table 1 Membrane Types and Pure Water Fluxes

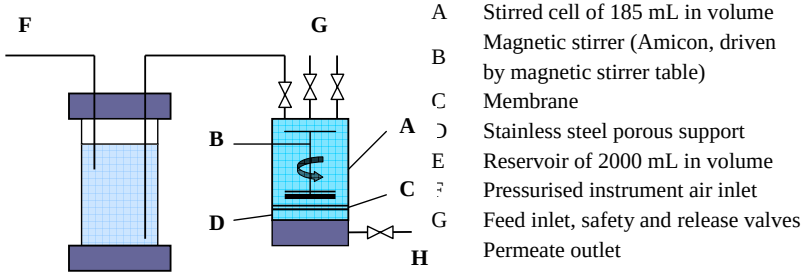
Membrane Type	Average Pure Water Flux* [$Lm^{-2}h^{-1}$]	Membrane resistance [m]	Membrane material
TFC-ULP	33.4 ± 6.7	$5.4 \cdot 10^{13}$	Polyamide on Polysulfon support
TFC-S	55.0 ± 7.3	$3.3 \cdot 10^{13}$	
TFC-SR1	52.6 ± 9.4	$3.4 \cdot 10^{13}$	
TFC-SR2	77.0 ± 25.2	$2.3 \cdot 10^{13}$	
X-20	19.2 ± 2.4	$9.4 \cdot 10^{13}$	Polyamide-urea Composite
ACM-4	25.8 ± 8.0	$7.0 \cdot 10^{13}$	
XN-40	42.5 ± 0.8	$4.2 \cdot 10^{13}$	
TS-80	26.0 ± 12.5	$6.9 \cdot 10^{13}$	

* Average values are derived from all experiments and variations are averaged.

Eight commercially available membranes were selected for this study, namely TFC-S, TFC-ULP, TFC-SR1, and TFC-SR2 supplied by Fluid Systems Cooperation, San Diego, CA and X-20, ACM-4, TS-80, and XN-40 supplied by Trisep Corporation. Membrane types, materials, pure water fluxes at 5 bar and membrane resistances are summarised in Table 1. It has been shown in our previous work that all membranes are negatively charged near pH neutral (Schäfer et al. (submitted B)).

Filtration System and Protocol

Experiments were carried out in a 185 mL stainless steel stirred cell. The inner diameter is 56.6 mm resulting in a membrane surface area of $21.2 \cdot 10^{-4}$ m^2. An Amicon magnetic stirrer was used and stirrer speed was fixed at 400 rpm to minimise polarisation concentration effects. Instrument grade air was used to pressurise the stirred cell. A schematic diagram is shown in Figure 1. A new membrane was used for each experiment.



A Stirred cell of 185 mL in volume
B Magnetic stirrer (Amicon, driven by magnetic stirrer table)
C Membrane
D Stainless steel porous support
E Reservoir of 2000 mL in volume
F Pressurised instrument air inlet
G Feed inlet, safety and release valves
H Permeate outlet

Figure 1: Filtration equipment

Each filtration experiment was conducted in three steps. The membrane was compacted for 1 hour using MilliQ water at 10 bar. Pure water flux was then determined at 5 bar. Next, the reservoir was emptied and the stirred cell filled with test solution. The solution was filtered at 5 bar, except for X-20, TS-80 and ACM-4 membranes which were operated at a pressure of 10 bar to obtain more comparable flux. Six permeate samples of 20 mL each were collected from a feed volume of 185 mL. A retentate sample was also collected for analysis. Parameters used to quantify the efficiency of a membrane separation process are flux (J) and solute retention (R) where the flux is defined as

$$J \equiv \frac{1}{A}\frac{dV}{dt} \qquad (1)$$

and retention as

$$R = 100 \cdot (1 - \frac{c_P}{c_B}). \qquad (2)$$

The adsorption of estrone on the membranes (Q_m) is quantified based on mass-balance, where the mass balance equation of is defined as

$$C_F V_F = Q_m + V_P \sum_1^6 c_{pi} + C_c V_c \qquad (3).$$

Membrane resistance is calculated as

$$R_M = \frac{\Delta P}{J \eta} \qquad (4).$$

Solution Chemistry and Chemicals

All chemicals were of analytical grade and were purchased from Ajax Chemicals (Australia). Estrone-2, 4, 6, 7-^{3}H(N) was purchased from Sigma-Aldrich (Saint Louis, Missouri, USA).

Secondary effluent was collected from Brendale Sewage Treatment Plant in Pine Rivers Shire, Queensland, Australia. Detailed characteristics of the secondary effluent are described in our earlier work (Schäfer et al, (submitted A)). The background electrolyte used consisted of 1 mM $NaHCO_3$, 0.5 mM $CaCl_2$ and 20 mM NaCl unless otherwise stated.

The effects of two types of natural organics on estrone retention were examined: (i) concentrated and freeze-dried surface water natural organic matter (NOM) and (ii) IHSS Suwannee River fulvic acid (FA). The FA is a purified reference material while the surface water has not been purified and thus contains a variety of organic compounds. The methods used to concentrate and characterize the surface water NOM have been described in detail elsewhere (Schäfer, 2001). Test solutions were prepared by adding NOM or FA to background electrolyte to make up solutions containing 10 mg/L as organic carbon of NOM or FA respectively.

Solutions were prepared by spiking estrone into five different matrices, namely MilliQ water, background electrolyte, secondary effluent and background electrolyte containing added NOM or FA. Feed concentration of estrone was 100 ng/L, an estrone concentration not atypical of surface waters and treated wastewaters.

Analytical Methods

The UV/VIS absorbance of samples were obtained using a Varian Cary 1E UV/VIS while a Perkin Elmer Optima 3000 Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) was used to determine cation content of the samples after digestion with 5% nitric acid. Estrone was analysed using a Packard Instruments scintillation counter. For this purpose, 9 mL of scintillation liquid was added to 1 mL of sample.

The extent of adsorption of estrone to the membranes was determined by the following procedure: At the end of each filtration experiment, the membranes were cut into small pieces and placed in a scintillation vial to which 5 mL of acetone was added. The vial was shaken vigorously and left for 1 hour for all estrone to dissolve. 1 mL of solution was then extracted into another vial which was air dried, redissolved with 1 mL of MilliQ water and 9 mL of scintillation liquid added prior to analysis.

RESULTS AND DISCUSSION

Adsorption of Estrone on Membranes

Assuming that the amount of estrone loss from the solution phase is equivalent to the amount of estrone adsorbed to the membrane, adsorption of estrone on the membrane can be calculated from mass balance considerations using equation (3). It can also be directly quantified using the analytical procedure described earlier. All values obtained from analytical measurement are plotted against values obtained from mass balance calculation in Figure 2. The overall difference between measured and calculated results is small. Indeed, an excellent correlation between analytically determined values and calculated values is observed. Where analytical and calculated values are found to be significantly different, we have assigned the extent of adsorption as the average of the two measured and calculated values.

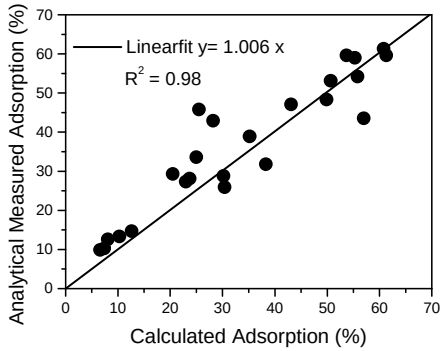


Figure 2: Analytical versus mass balance calculated adsorption of estrone to membranes.

Retention results in MilliQ water are shown in Table 2. The amount of material lost, presumably as a result of adsorption to the membrane, is calculated using mass-balance and also presented in Table 2. In MilliQ water, retention of estrone for all membranes is more than 97% except for the XN40 membrane for which it is 82 %. However, adsorption of estrone to the membrane varies significantly ranging from 0 to 12.2 ng, corresponding to 0 to 66.0%.

As membrane resistance increases, adsorption decreases (see Figure 3). Strong correlation between adsorption and membrane resistance has been found for all membranes, except the TS-80 membrane. This can be explained by diffusion model developed by Chen et al. (2001). Low membrane resistance results in higher mass flux of estrone into the membrane, hence a higher adsorption is observed. As a result of adsorption, retention of estrone for low resistance membrane remains high. Another possibility is the back diffusion – convection relationship. A higher flux increases the boundary layer concentration unless back diffusion is very fast, which is not to be expected. An increased concentration is likely to increase adsorption.

Table 2: Retention (and calculated adsorption) of estrone to various membranes in MilliQ water (pH 6, no salt)

Membrane Type	Estrone Retention [%]	Estrone Adsorption from Mass Balance Calculation [ng]
TFC-ULP	98.7	0.99
TFC-S	98.7	10.15
TFC-SR1	98.3	10.10
TFC-SR2	97.6	12.21
X-20	98.6	0.00
ACM-4	99.1	0.66
XN-40	81.6	5.97
TS-80	98.8	6.69

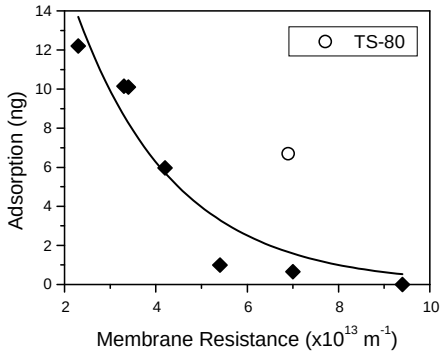


Figure 3: Relationship between adsorption and membrane resistance.

Many researchers have shown that hydrophilicity of the membrane results in lower adsorption (Childress, 1996). Surprisingly, TFC-SR1 and TFC-SR2 have high adsorption values despite of their highest hydrophilicity (results of contact angle measurements are described by Schäfer et al. (submitted B). Adsorption due to H-bonding can dominate and outweigh the hydrophobic effect. A number of researchers have attempted to use H-bonding between functional groups of membrane and solute to explain adsorption behaviour of solutes on the membrane (Williams, 1999; Schäfer et al. (submitted B)). In fact, the hydrophilicity of the membrane can augment the formation of H-bonding.

Adsorption in buffer solution

Table 3: Adsorption & retention in buffer solution (pH 7.8, 20 mM NaCl, 1 mM $NaHCO_3$, 0.5 $CaCl_2$)

Membrane Type	Estrone Retention [%]	Estrone Adsorption [ng]	
		Analytical Measure	Mass-Balance Calculation
TFC-ULP	95.9	5.59	5.32
TFC-S	98.1	4.38	5.20
TFC-SR1	92.8	9.94	11.03
TFC-SR2	79.2	9.38	9.82
X-20	99.3	1.37	1.90
ACM-4	86.1	4.72	8.48
XN-40	73.1	4.63	6.22
TS-80	83.2	5.22	7.94

To study the influence of a salt matrix solution, a new series of experiments was set up with $CaCl_2$ and NaCl added to MilliQ water to make up a solution contained 0.5 mM $CaCl_2$, 20 mM NaCl and 1 mM $NaHCO_3$ at pH ≈ 7.8. This is corresponding to ionic strength of 0.0225 M. To verify the integrity of the quantification of adsorption using the mass balance approach, adsorption was also quantified using an analytical procedure as described earlier. Other studies have shown that the presence of mono-valent and di-valent ions affects membrane characteristics, performance as well as organics characteristics (Braghetta et al. 1997; Schäfer, 2001). As expected, some change in adsorption was observed. Retention for all membranes has decreased by up to 15 % compared to the MilliQ water matrix, except TFC-S and X-20. This suggests that the removal of estrone by the relatively tight TFC-S and X-20 membranes is dominated by size exclusion, and consequently adsorption occurs mostly on the surface of the active skin layer. The decrease in retention cannot be explained, however the salt concentration may change the adsorptive interactions between membranes and estrone.

Adsorption in natural water and secondary effluent

Estrone retention, adsorption and UV $_{254nm}$ retention in natural water, in synthetic fulvic acid solution and in secondary effluent are shown in Table 4, Table 5 and Table 6, respectively. In general, TFC membranes adsorb more estrone than others. This is consistent with our previous contention as they are low resistance membranes and the flux is higher. Estrone adsorption in natural water and secondary effluent is similar and slightly lower than that in fulvic acid. FA is a purified reference material, while both secondary effluent and NOM are unpurified and contain low

molecular weight acids, which may facilitate transport of estrone through the membranes. The presence of matrix compounds such as organics influences the composition of the boundary layer and most likely also the back diffusion of estrone into the bulk.

However, while adsorption changes considerably due to the presence of organics in the feed solution, retention does not respond to the same extent. According to a model on the transport of small molecules penetrating into dense membranes due to diffusion developed by Chen et al. (2001), transport behaviour can be classified into three categories : (i) Fickian diffusion, in which the rate of diffusion is much less than that of sorption. (ii) Sorption control process, in which the diffusion rate is much faster than that of sorption. (iii) Non-Fickian or anomalous diffusion, which occurs when diffusion rate and the sorption rate are comparable. If Fickian diffusion occurs, increase in adsorption leads to increase in retention. If sorption control process or non-Fickian diffusion occurs, increase in adsorption leads to decrease in retention (Chen et al, 2001). There is no clear correlation between adsorption and retention. This suggests that adsorption may occur based on other mechanisms including ion exchange and specific interactions, depending on the specific membrane, and the influence of adsorption on retention is membrane dependant. The effect of adsorption on retention needs to be investigated on the membranes individually.

Table 4: Adsorption and retention in NOM solution (10 mgL^{-1} NOM as organic carbon, pH 7.8, 20 mM NaCl, 1 mM $NaHCO_3$, 0.5 $CaCl_2$)

Membrane Type	Ca/Na Retention [%]	J_F/J_{W0}	Estrone Retention [%]	Estrone Adsorption [ng]		UV $_{254nm}$ Retention [%]
				Analytical Measure	Mass-Balance Calculation	
TFC-ULP	57.6/46.5	0.80	90.4	7.97	8.71	93.5
TFC-S	88.2/72.5	0.68	94.4	5.62	4.79	96.2
TFC-SR1	54.6/24.4	1.09	95.9	11.25	11.34	97.2
TFC-SR2	67.6/31.0	1.00	88.3	10.32	10.03	98.4
X-20	95.2/90.6	0.72	95.7	1.22	1.83	98.5
ACM-4	95.9/91.5	0.95	96.6	1.50	2.33	98.6
XN-40	39.8/27.3	0.87	73.2	7.09	5.88	97.2
TS-80	95.1/88.4	0.74	97.4	1.91	2.46	98.7

Large natural organic molecules can deposit onto the membrane surface causing flux decline and increase in solutes retention (Childress and Deshmukh, 1998; Schäfer et al. 2000). However, as the membrane, natural organics and fulvic acid are all negatively charged, minimal deposition of organics is expected to occur due to the electrostatic repulsion between the membrane surface and the organic matter. Some extent of flux decline is observed, but it is mostly because of osmotic pressure effects due to salt retetnion. Organic matter influences charge and hydrophobicity of the membrane, thus adsorption of mircro-comtaminants on the membrane. Adsorption of estrone on the most hydrophilic TFC-SR1 and TFC-SR2 membranes is consistently high at approximately 10.5 ng, corresponding to about 60 % of the initial mass in the feed solution. Note that a similar pattern was observed for the MilliQ and buffer matrices. It appears as if adsorption for those membranes is independent of the matrix compounds indicating a strong affinity. Consistently, XN-40 has the lowest estrone retention, although adsorption is reasonably high. This is possibly because XN-40 has less interactive sites for adsorption and the largest pores, so molecules can pass through the

membrane without a very close contact with the pore surface. For other membranes, although retention is similar in general, adsorption is found to vary depending on the matrix compounds.

Table 5: Adsorption and retention in FA solution (10 mgL^{-1} FA as organic carbon, pH 7.8, 20 mM NaCl, 1 mM $NaHCO_3$)

Membrane Type	Ca/Na Retention [%]	J_F/J_{W0}	Estrone Retention [%]	Estrone Adsorption [ng]		UV $_{254nm}$ Retention [%]
				Analytical Measure	Mass-Balance Calculation	
TFC-ULP	-/62	0.76	89.5	10.55	8.05	96.7
TFC-S	-/80	1.00	95.5	6.51	7.20	97.7
TFC-SR1	-/25	1.22	94.5	10.23	10.92	98.9
TFC-SR2	-/37	1.13	86.9	11.34	11.03	98.4
X-20	-/80	0.73	97.8	3.79	7.03	97.6
ACM-4	-/65	0.78	97.5	4.26	8.73	96.1
XN-40	-/24	0.97	76.2	9.23	8.94	97.9
TS-80	-/93	0.80	93.5	2.33	2.72	98.1

Table 6: Adsorption and retention in secondary effluent

Membrane Type	Ca/Na Retention [%]	J_F/J_{W0}	Estrone Retention [%]	Estrone Adsorption [ng]		UV $_{254nm}$ Retention [%]
				Analytical Measure	Mass-Balance Calculation	
TFC-ULP	84/72	0.90	96.5	-	8.16	97.2
TFC-S	98/85	0.77	98.5	-	2.61	95.8
TFC-SR1	75/34	1.19	92.9	-	10.64	97.2
TFC-SR2	40/8	1.02	85.8	-	10.53	85.2
X-20	94/86	0.91	92.3	-	3.27	92.4
ACM-4	89/82	0.62	77.0	-	3.74	96.0
XN-40	60/38	0.87	77.9	-	6.64	83.5
TS-80	95/82	0.82	91.2	-	2.57	93.8

CONCLUSIONS

The adsorption properties of estrone on NF and RO membranes were investigated in this study. It was shown that estrone was adsorbed on the membranes to a large extent and retention of estrone was high for all membranes. Increase in membrane resistance can result in decrease in adsorption of estrone. It appears that adsorption of estrone by some membranes is influenced by the matrix of the feedwater. This has a strong implication on the use of NF and RO for trace organics removal, since release of absorbed organics may occur when the chemistry of solution changes and retention may be limited to available adsorbent sites. Adsorption may occur based on different mechanisms depending on the membranes, and further studies on individual membranes will be carried out to investigate the mechanisms of adsorption and retention in detail.

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SYMBOLS

A:	Membrane Surface [m^2]	R:	Retention [%]	J_F:	Solution flux [$Lm^{-2}h^{-1}$]
c_B:	Bulk Concentration [mgL^{-1}]	R_M:	Membrane Resistance [m^{-1}]	J_{wo}:	Pure water flux [$Lm^{-2}h^{-1}$]
		t:	Time [h]	η:	Dynamic viscosity of water [Pa s]
c_P:	Permeate Conc. [mgL^{-1}]	V:	Permeate Volume [L]		
J:	Flux [$Lm^{-2}h^{-1}$]	Q_m:	Adsorption on the membrane [ngL^{-1}]		
ΔP:	Pressure [bar]				

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